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STANNOUS DOUBLE HALIDE SALTS

WITH A FEW NOTES UPON THE

CUPROUS DOUBLE HALIDE SALTS.

DISSERTATION

PRESENTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

GEORGE M. RICHARDSON.

1890.

BALTIMORE:
PRESS OF ISAAC FRIEDENWALD,
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The crystallographic portion of the work was done under the direction of Prof. George H. Williams, for whose advice and kind assistance I wish also to express my gratitude.

STANNOUS DOUBLE HALIDE SALTS.

Introduction.

The existence of the so-called *double chlorides, double bromides*, and *double iodides* has long been well known to chemists. These compounds do not differ in any essential respect from other chemical compounds, but their constitution cannot be explained by the prevailing views of valence, and hence they have been termed *double salts*, or *molecular compounds*, and thus an artificial distinction made between them and *atomic* or *true* chemical compounds. As a result of this distinction the double salts have been comparatively little studied. This very large and constantly growing class of compounds has, however, attracted the attention of a number of chemists, who have from time to time made suggestions concerning their probable constitution. These suggestions have produced but little effect, since they introduced new ideas concerning the valence of the elements present in the compound.

As early as 1826 Von Bonsdorff[1] pointed out that there existed acid and basic chlorides analogous to the acid and basic oxides, and that these chlorides could unite with one another forming salts of the third order, just as the oxides were supposed to do. Boullay[2] was of the same opinion; and Bolley[3] recognised the justice of Von Bonsdorff's idea. But this view was opposed by Liebig,[4] Berzelius,[5] and other chemists, since they considered the chlorides themselves as salts analogous to other salts of the third order, and hence, as they believed, they could not have acid or basic properties.

Naquet[6] was the first to suggest, in 1867, that the molecules in the double chlorides might be united by means of their chlorine atoms.

Blomstrand[7] put forth the same view, and has shown that two

[1] Ann. chim. phys. **34**, 142. [2] Ibid. **34**, 337. [3] Liebig's Ann. **39**, 100.
[4] Ann. chim. phys. **35**, 68. [5] Berz. Jahrsb. **8**, 138.
[6] In his Principes de Chimie fondée sur les Theories Modernes. Paris, 1867, p. 62.
[7] In his Chemie der Jetztzeit, p. 340.

chlorine atoms appear to exercise some of the functions of an oxygen atom.

Similar views have been expressed by Jörgensen,[1] Mallet,[2] Armstrong,[3] Franke,[4] Heyes,[5] and others. Gibbs[6] has suggested that in such compounds as KHF_2 the potassium is trivalent; and Williamson[7] has cited the compounds K_2CuCl_4, K_2HgCl_4, etc., to prove that copper, mercury, etc., may act as hexavalent elements under certain conditions.

None of these views have met with general acceptance, as the evidence presented for them did not seem convincing. Prof. Remsen[8] has recently called attention to the views of Naquet and Blomstrand, and has pointed out how the facts support these views; he shows very clearly the strong analogy which exists between these compounds and the corresponding oxygen salts; and finally he gives a law which governs the composition of these bodies. The law is thus stated:

When a halide of any element combines with a halide of an alkaline metal to form a double salt, the number of molecules of the alkali salt which are added to one molecule of the other halide is never greater, and is generally less, than the number of the halogen atoms contained in the latter.

There have been described, however, a few salts which are exceptions to this rule.

For example:

$SnCl_2.4KCl.3H_2O$[9]
$CuCl.2KCl$[10]
$MnF_2.4KF$
$BiCl_3.6CsCl$[12]
$PbI_2.4KI$[13].

If these exceptions are well established it is evident that the rule is incorrect. But the exceptions are so few, while the number of compounds which are formed according to this rule is so great, that it seems desirable to prepare these exceptional salts, if they really can be formed, and to study them very carefully to learn

[1] J. prakt. Chem. **16**, 352.
[2] Am. Chem. J. **3**, 189.
[3] British Assoc. Repts. 1885, 959.
[4] J. prakt. Chem. N. F. **36**, 451 (1887).
[5] Phil. Mag. **25**, 221, 297.
[6] Am. J. Sci. **44**, 409 (1867).
[7] British Assoc. Repts. 1881, 577.
[8] Am. Chem. J. **11**, 291.
[9] Poggiale: J. prakt. Chem. **35**, 329.
[10] Mitscherlich: Ann. chim. phys. **73**, 1840, 384.
[11] Nickles: Bull. Soc. Chim. [2] **8**, 408 (1867).
[12] Godeffroy: Berichte **8**, 9.
[13] Boullay: Ann. chim. phys. [2] 1827, **34**, 370.

whether or not they have any peculiarities besides that of their composition which would distinguish them from the other double salts.

With this object in view, the writer undertook to prepare and study the stannous salt described by Poggiale, and in connection with it, the other double stannous salts that are formed with potassium and ammonium.

The results of this study form the subject of this paper, and will now be given in detail.

Compounds of Stannous Chloride and Potassium Chloride.

In addition to the salt $SnCl_2.4KCl.3H_2O$, the salt $SnCl_2.2KCl$ is mentioned in the larger works upon chemistry, but there seems to be some confusion concerning it.

Graham has spoken of the salt $SnCl_2.2KCl.3H_2O$. Mitscherlich in his text-book speaks of the salt $SnCl_2.2KCl.2H_2O$.

Apjohn has described the salt $SnCl_2.2KClH_2O$, and stated that it crystallised in octahedra.

Rammelsberg has analysed[1] and measured[2] an orthorhombic salt to which he assigns the formula $SnCl_2.2KClH_2O$, and says further that the octahedra obtained by Apjohn were probably the stannic salt $SnCl_4.2KCl$. This salt is frequently formed along with the stannous salt. Marignac[3] confirmed the results of Rammelsberg.

The double halides here described were prepared, in most cases, by mixing the solutions of the constituent halides. The alkaline halide was dissolved in water, and the tin solution was made by dissolving tin in hydrochloric acid or hydrobromic acid, having an excess of tin present to prevent the presence of free acid in the solution.

Mono-potassium chloro-stannite, $KSnCl_3H_2O$.—When a solution of potassium chloride is mixed with a solution of stannous chloride in such proportions that the stannous chloride is present in large excess, white, hair-like crystals will form after a time, or if the solutions are nearly saturated will form at once. These crystals, carefully dried by pressing between drying papers, were analysed with the following results:

[1] Pogg. Ann. **94**, 507. [2] In his Krystal Chemie, p. 211. [3] Jahrsber. 1857, 221.

	Found.	Calculated.
Sn	41.60 per cent.	41.91 per cent.
K	14.09	13.88
Cl	38.15	37.82
H_2O	5.88	6.39
	99.72	100.00

From which it would appear that the formula is $SnCl_2KClH_2O$ or $KSnCl_3H_2O$.

This salt is quite stable in the air, it does not lose its water of crystallisation over sulphuric acid, but loses it at 100°, without suffering further change. Heated to high temperatures it loses hydrochloric acid with its water of crystallisation, and is thus decomposed, oxides of tin being formed. The salt is decomposed by water, forming a turbid solution; it dissolves, forming a clear solution, in hot hydrochloric acid or in a hot solution of potassium chloride, but from both of these solutions there crystallises out upon cooling a salt having the composition $SnCl_2.2KCl.2H_2O$ or $K_2SnCl_4.2H_2O$.

Di-potassium chloro-stannite, $K_2SnCl_4.2H_2O$.—If, instead of having the stannous chloride present in large excess, the solutions are mixed in about equal portions or the potassium chloride is present in excess, large, opaque, white, orthorhombic crystals are formed after standing for a time. The crystals, carefully dried and analysed, gave the following results:

	Found.		Calculated.
	A.	B.	
Sn	31.54 per cent.	31.46 per cent.	31.55 per cent.
K	20.64	21.48	20.86
Cl	38.54	37.59	37.97
H_2O	9.37	10.47	9.62
	100.09	101.00	100.00

This would indicate that the formula is $K_2SnCl_4.2H_2O$. This salt is perfectly stable in the air. A sample which had been exposed to the action of the atmosphere for forty days gave with ferric chloride and standard permanganate solution 31.49 per cent. of stannous tin, the theory being 31.55 per cent. It does not lose its water of crystallisation over sulphuric acid, but gradually loses the whole of it at 100° without change. It may be recrystallised without change from hydrochloric acid, being quite soluble

in the hot acid and comparatively insoluble in the cold acid. It may also be recrystallised from a potassium chloride solution without change of composition; the habit of the crystals formed in the two cases is quite different; from the hydrochloric acid they are much elongated, parallel to the C axis, and rarely have terminal planes, while from the potassium chloride solution they are less elongated and the terminal planes are well formed.

Di-potassium chloro-stannite, $K_2SnCl_4H_2O$.—When large quantities of the salt just described, $K_2SnCl_4.2H_2O$, are dissolved in hot hydrochloric acid and the solution quickly cooled, there is a white crystalline precipitate formed, and after a few moments crystals of the salt $K_2SnCl_4.2H_2O$ begin to grow, and increase in size with great rapidity. If this crystalline precipitate is removed before the crystals of the second salt begin to form, and is analysed, it is found to have the formula $K_2SnCl_4H_2O$, that is, it differs by one molecule of water of crystallisation from the large crystals.

The following results were obtained by analysis:

	Found.	Calculated.
Sn	33.05 per cent.	33.15 per cent.
K	21.48	21.91
Cl	39.11	39.89
H_2O	...	5.05
		100.00

This salt also is stable in the air, but if left in its mother-liquor it gradually takes up more water of crystallisation and is transformed into the salt $K_2SnCl_4.2H_2O$. Its does not lose its water of crystallisation over sulphuric acid, but loses it at 100°. If this salt or the one with two molecules of water be dissolved in hot stannous chloride solution, the salt $KSnCl_3H_2O$, already described, crystallises out on cooling.

All efforts to prepare other salts composed of stannous chloride and potassium chloride than those just described have proved fruitless. The salt $K_2SnCl_4.2H_2O$ was dissolved in potassium chloride solution in the hope of getting the salt described by Poggiale, but in vain; the salt $K_2SnCl_4.2H_2O$ was again obtained and the excess of potassium chloride crystallised out by itself.

The solutions were mixed so that a large excess of the potassium was present, but with the same result, the potassium chloride

in excess of that required for the salt $K_2SnCl_4.2H_2O$ crystallised out alone, usually crystallising in transparent octahedra.

The mother-liquors from these crystals were evaporated and a second and third crop of crystals obtained, but always with the same result, viz., $K_2SnCl_4.2H_2O$. By the evaporation there were also formed octahedra of the well-known stannic salt K_2SnCl_6 or $SnCl_4.2KCl$, since the evaporation of the solutions oxidises the tin, probably according to the equation

$$3SnCl_2 + O = SnCl_4 + Sn_2OCl_2.$$

When a saturated solution of stannous chloride is added to a saturated solution of potassium chloride, crystals form very rapidly, and so completely fill the vessel in a few moments that it may be inverted without loss of the solution. An examination of this mass proves it to consist of all three of the salts above described, but upon standing a few days, if sufficient potassium chloride is present, it will be entirely converted into the salt $K_2SnCl_4.2H_2O$, otherwise there will remain a mixture of the two salts $K_2SnCl_4.2H_2O$ and $KSnCl_3H_2O$; the latter salt appears to be stable only in the presence of a considerable excess of stannous chloride if allowed to remain in the solution from which it has crystallised. So also, as we have seen, the salt $K_2SnCl_4H_2O$ will take up an additional molecule of water if it is allowed to stand in its mother-liquor for several days; but if it is removed before long standing it is possible to get a mass of crystals of $K_2SnCl_4.2H_2O$, which are in a matrix of the salt $K_2SnCl_4H_2O$.

Compounds of Stannous Chloride and Ammonium Chloride.

The salts thus composed which have been described in the chemical text-books and journals are the same, as for the corresponding potassium compounds, in every way.

Mono-ammonium chloro-stannite, $NH_4SnCl_3H_2O$.—This salt is prepared just as the corresponding potassium salt is prepared, and as far as it has been studied it is analogous to the potassium salt in every respect, with the exception that the tendency to pass over into the orthorhombic form is here even more marked than in the case of the potassium salt.

Di-ammonium chloro-stannite, $(NH_4)_2SnCl_4.2H_2O$.—This salt is very readily obtained by bringing the solutions of the component

chlorides together and allowing them to stand. The crystals are isomorphous with the corresponding potassium salt, which it resembles in its general properties. The tin and water were determined in this salt with the following results:

	Found.	Calculated.
Sn	35·54 per cent.	35·58 per cent.
H_2O	9·95	10.84

This proves its formula to be $(NH_4)_2SnCl_4.2H_2O$.

All efforts to prepare the salt with one molecule of water of crystallisation, $(NH_4)_2SnCl_4H_2O$, analogous to the potassium salt $K_2SnCl_4H_2O$, have been unsuccessful.

Crystals of the salt $(NH_4)_2SnCl_4.2H_2O$ and of the salt $K_2SnCl_4.2H_2O$ have been measured[1] and they are found to be the same as those measured by Rammelsberg,[2] yet he ascribes to them the composition represented by the formulæ $(NH_4)_2SnCl_4H_2O$ and $K_2SnCl_4H_2O$. For the potassium salt he gives the following analysis:[3]

	Found. A.	Found. B.	Calculated.
K	23.07 per cent.	22.79 per cent.	22.00 per cent.
Sn	33.32	33.58	33.07
Cl	...	...	39.87
H_2O	...	...	5.06

From these results it would appear that Rammelsberg had measured one salt and analysed another; this is not improbable, since they may both occur in the same crystal mass.

But how is it with regard to the ammonium salt? We have seen that the ammonium salt with one molecule of water of crystallisation cannot be prepared, so that it would be impossible to make a similar mistake here.

He obtained by analysing his ammonium salt the following results:[4]

	Found.	Calculated.
NH_4	10.24 per cent.	11.49 per cent.
Sn	35·93	37·52
Cl	44·39	45·25
H_2O	...	5·74

[1] See crystallographic measurements, pages 19 and 20 of this paper.
[2] In his Krystal Chemie, 211 and 212. [3] Pogg. Ann. **94**, 510. [4] Pogg. Ann. **94**, 510.

From this analysis he assigned to the salt the formula $(NH_4)_2SnCl_4H_2O$. But the calculated results for the formula with two molecules of water are:

NH_4	10.84 per cent.
Sn	35.54
Cl	42.78
H_2O	10.84
	100.00

These calculated results agree more closely with Rammelsberg's analysis than do the results calculated from the formula which he assigns to the salt, so that his own analysis proves that the formula for the ammonium compound at least is $(NH_4)_2SnCl_4.2H_2O$ and not $(NH_4)_2SnCl_4H_2O$.

Poggiale in describing the salts $SnCl_2.4KCl.3H_2O$ and $SnCl_2.4NH_4Cl.3H_2O$ gives no analyses, but says that the salts were obtained directly from a mixture of the solutions in beautiful long needles. The salts he really obtained were in all probability $K_2SnCl_4.2H_2O$ and $(NH_4)_2SnCl_4.2H_2O$, or as they are usually written $SnCl_2.2KCl.2H_2O$ and $SnCl_2.2NH_4Cl.2H_2O$.

The Action of Stannous Chloride upon Sodium Chloride and Lithium Chloride.—If saturated solutions of stannous chloride and sodium chloride be mixed no crystals are formed. If the solution be evaporated or allowed to stand over sulphuric acid for a long time the solution becomes thick and oily, and finally after the volume of the liquid has been much reduced sodium chloride crystallies out alone.

Lithium chloride behaves in the same way.

Compounds of Stannous Bromide and Potassium Bromide.

Very little is said of these compounds in the text-books and journals. They are spoken of only in connection with the chlorides, and are said to be similar to them.

Mono-potassium bromo-stannite, $KSnBr_3H_2O$.—Upon adding a solution of potassium bromide to a solution of stannous bromide, almost instantly, if the solutions are concentrated, bundles of long hair-like crystals are formed, and grow with great rapidity until the vessel is quite filled with them. These crystals were analysed with the following results:

	Found.	Calculated.
Sn	27.77 per cent.	28.43 per cent.
H_2O	4·35	4·34

This salt is similar in appearance to the corresponding chloride, and like it is quite stable in the air, retains its water of crystallisation over sulphuric acid, but loses it at 100° without change of the salt. But it differs from the chloride in being much more readily formed from the mixed solutions, being formed even in the presence of an excess of potassium bromide. It may be recrystallised from hydrobromic acid, and even from a solution of potassium bromide.

Di-potassium bromo-stannite, $K_2SnBr_4.2H_2O$.—As just seen, when solutions of stannous bromide and potassium bromide are mixed the salt $KSnBr_3H_2O$ is always formed, but if there is present an excess of potassium bromide, or if the salt $KSnBr_3H_2O$ be dissolved in a solution of potassium bromide, and the crystals which separate out on cooling allowed to stand several days in the solution, it will be found that large orthorhombic crystals are scattered through the mass of the other crystals.

This salt is similar to the corresponding chloride in its general appearance and in its properties. An analysis of the crystals led to the results that follow, proving its formula to be $K_2SnBr_4.2H_2O$.

	Found.	Calculated.
Sn	21.08 per cent.	21.38 per cent.
H_2O	6.12	6.52

The salt cannot be recrystallised from its solutions in hydrobromic acid; if it is dissolved in this acid the salt $KSnBr_3H_2O$ crystallises out. A salt with one molecule of water of crystallisation analogous to the chloride $K_2SnCl_4H_2O$ was not obtained.

Compounds of Stannous Bromide and Ammonium Bromide.

Mono-ammonium bromo-stannite, $NH_4SnBr_3H_2O$.—Upon mixing the solutions of stannous bromide and ammonium bromide the hair-like crystals of $NH_4SnBr_3H_2O$ are at once formed. In its general properties this salt is like other similar salts already described; it differs from the corresponding chloride, $NH_4SnCl_3H_2O$, in that it is much more readily formed from the mixed solutions, and it differs from the corresponding potassium salt, $KSnBr_3H_2O$, in being less readily formed from the mixed solutions, and in passing more readily over into the orthorhombic variety.

Di-ammonium bromo-stannite, $(NH_4)_2SnBr_4.2H_2O$.—Crystals of this salt may be obtained by mixing the two solutions so that ammonium bromide is present in excess and allowing the salt $NH_4SnBr_3H_2O$ which is at first formed to stand, when crystals of the salt $(NH_4)_2SnBr_4.2H_2O$ are obtained. It resembles the other similar salts already described. Analysis of the crystals gave:

	Found.		Calculated.
	A.	B.	
Sn	23.00 per cent.	22.97 per cent.	23.14 per cent.
H_2O	6.34		7.06

Crystals of this salt are more readily obtained than the crystals of the salt $K_2SnBr_4.2H_2O$, but are not so easily obtained as either of the chlorides $K_2SnCl_4.2H_2O$ or $(NH_4)_2SnCl_4.2H_2O$.

Compounds containing Chlorine and Bromine.

Compounds of Stannous Bromide with Potassium Chloride.—When a solution of potassium chloride is added to a solution of stannous bromide, the hair-like crystals are formed, just as when the two chlorides or the two bromides are mixed, and it was thought from analogy that the salt $KSnBr_2ClH_2O$ or $SnBr_2KClH_2O$ was formed, but upon analysis it was found not to yield constant results. Several specimens of this salt were prepared, and the tin they contained was determined as follows:

Sample A gave 28.63 per cent. Sn.
B " 29.66
C " 31.19
D " 30.04
E " 29.21

The calculated percentage of tin in a salt having the formula $SnBr_2KClH_2O$ is 31.84 per cent.; possibly different salts are formed as follows:

$$4SnBr_2 + 4KCl + 4H_2O = \begin{cases} SnBr_2KBrH_2O & (1) \\ 2)\ SnBr_2KClH_2O & (2). \\ SnCl_2KBrH_2O & (3) \end{cases}$$

The calculated amounts of tin in these salts is, (1) 28.43 per cent.; (2) 31.84 per cent.; (3) 36.18 per cent.

Or more probably it is a mixture of the two salts $KSnBr_3H_2O$ and $KSnCl_3H_2O$, the former being present in excess, as we should

expect, since we have seen that it is much more readily formed than the latter. The percentage of tin in these two salts is:

$$KSnBr_3H_2O = 28.43$$
$$KSnCl_3H_2O = 41.91.$$

But in order to determine this point, further investigation is necessary.

A similar mixture is obtained when potassium bromide solution is added to stannous chloride solution. The same is true of solutions of ammonium chloride and stannous bromide, or if ammonium bromide and stannous chloride are mixed.

When the alkaline halide is added in excess, orthorhombic crystals are formed.

An analysis of some of the crystals formed by adding potassium chloride to stannous bromide led to the formula $K_2SnCl_2Br_2.2H_2O$. The results of the two analyses are as follows:

	Found: A.	B.	Calculated.
Sn	25.63 per cent.	25.48 per cent.	25.49 per cent.
K	17.21	17.17	16.85
Br	36.60	36.70	34.56
Cl	15.46	14.94	15.33
H_2O	4.60	...	7.77
	99.50		100.00

Similar crystals were made by mixing the solutions of stannous chloride and potassium bromide, and these were analysed with the following results:

	Found.
Sn	24.18 per cent.
K	16.66
Br	34.43
Cl	15.27
H_2O	8.01
	98.55

which leads to the same formula, $K_2SnCl_2Br_2.2H_2O$, as assigned to the crystals prepared from stannous bromide and potassium chloride.

These crystals could not be distinguished from one another in any of their properties.

These crystals, when heated in a current of dry air, first lose water with some hydrochloric acid and some hydrobromic acid, with the formation of oxychloride and oxybromide of tin; then stannous chloride and stannous bromide sublime and are deposited in the cooler parts of the tube, leaving behind a mixture of potassium chloride, potassium bromide, tin oxychloride, and tin oxybromide. If the water be first driven off at 100° and the dried salt heated in a current of dry hydrogen, the stannous bromide and chloride sublime, leaving potassium bromide and chloride behind. There is also a slight reduction of the tin to the metallic state, and both hydrochloric and hydrobromic acids are given off.

The angles of these two series of crystals appear to be the same, but the faces gave such poor reflections and so many images that accurate measurements could not be made. With the hope of getting better crystals, several more specimens of the salt were prepared from solutions of different strengths. Upon analysis these new specimens were found to contain varying amounts of tin.

Specimen A gave 25.04 per cent. of Sn.
B " 25.71
C " 26.02
D " 26.59
E " 27.34
F " 26.94

The faces of these crystals also gave poor reflections and multiple images, yet a variation in angle could be detected in the crystals of different composition.

In the case of the ammonium salt the reflections are much better and the crystals can be very accurately measured. The crystals from different solutions are found to vary in their angles and upon analysis are found to be of variable composition. A determination of tin in four different specimens resulted as follows:

Specimen A gave 24.29 per cent. of Sn.
B " 24.42
C " 25.20
D " 25.56

The calculated amount of tin in a compound having the formula $(NH_4)_2SnBr_2Cl_2.2H_2O$ is 28.03 per cent. These results suggest an isomorphous mixture of the chloride molecule and the bromide

molecule. If this is the case it ought to be possible to get crystals varying in their percentage of tin from 21.38 per cent. in the case of the pure $K_2SnBr_4.2H_2O$ molecule to 31.55 per cent. in the case of the pure $K_2SnCl_4.2H_2O$ molecule, and from 23.14 per cent. to 35.55 per cent. in the case of the ammonium salts. A further study of these salts will be carried out in order to determine the amount of change in angle measurement that accompanies a given change in composition, and to decide, if possible, whether or not the molecule $K_2SnCl_2Br_2.2H_2O$ exists or whether it would be better expressed by the formula $K_2SnCl_4.2H_2O + K_2SnBr_4.2H_2O$; the latter at present seems the more probable.

R. W. Atkinson[1] has prepared the salt $K_3SbCl_3Br_3.1\frac{1}{2}H_2O$ by mixing antimony chloride and potassium bromide, and the same salt by mixing potassium chloride with antimony bromide. And R. H. Solly[2] has proved their crystallographic identity. Atkinson also obtained crystals to which he gives the formula $Sb_2Cl_6Br_3K_3.2H_2O$ and $SbCl_3BrKH_2O$; he does not speak of having any difficulty in obtaining pure specimens.

Summary of the Stannous Salts.

We have seen that stannous chloride and bromide form two classes of salts with potassium and ammonium bromide and chloride. One class contains one molecule of the alkaline halide, and the other class contains two molecules of the alkaline halide. In the case of the chlorides the tendency to form the salt with two molecules of the alkaline chloride is very strong, and is even more marked with the ammonium chloride than with the potassium chloride. With the bromides on the other hand the tendency is to form the salt with one molecule of the alkaline bromide, while the one with two molecules of the alkaline bromide is obtained with greater difficulty, and here too the salt with two molecules of ammonium bromide is much more readily obtained than the potassium salt is.

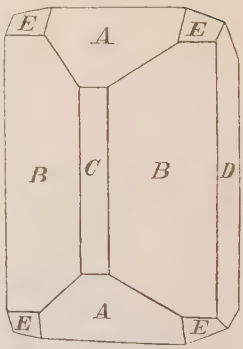
The salts of lithium and sodium, if formed at all, are so soluble that they cannot be crystallised.

From this it is seen that tin *does not* yield any salts that are exceptions to the rule put forward by Prof. Remsen.

[1] Jour. Chem. Soc. **43** (1883), 289. [2] Ibid. 293.

Crystallographic Examination of Salts.

We have seen that the salts $K_2SnCl_4.2H_2O$, $(NH_4)_2SnCl_4.2H_2O$, $(NH_4)_2SnBr_4.2H_2O$, $K_2SnBr_4.2H_2O$ are all orthorhombic in their crystallisation and that they have the same habit, the most general form being that shown in the figure, in which



$A = P\bar{\infty}$
$B = \infty P$
$C = \infty P\bar{\infty}$
$D = \infty P\breve{\infty}$
$E = P$

Most of the crystals consist simply of the two forms ∞P and $P\bar{\infty}$, others are modified by $\infty P\bar{\infty}$ and $\infty P\breve{\infty}$ and rarely P. The salt $K_2SnBr_4.2H_2O$, however, rarely has the $P\bar{\infty}$ developed, but is terminated by P instead.

In the following observations the faces of the crystals are classified as *poor* (p), *fair* (f), *good* (g), or *very good* (v. g.) according to the clearness of the reflected image which they give. In making up the means of the observations the different observations were given different weight according to the perfectness of the reflected image.

The following weights were assigned to the different observations:

2 poor images have a weight of 1.
1 poor image and 1 fair image have a weight of 2.
1 poor image and 1 good image have a weight of 3.
1 poor image and 1 very good image have a weight of 4.
2 fair images have a weight of 5.
1 fair image and 1 good image have a weight of 6.
1 fair image and 1 very good image have a weight of 7.
2 good images have a weight of 8.
1 good image and 1 very good image have a weight of 9.
2 very good images have a weight of 10.

The means where each observation has the same weight are also calculated for comparison.

But for calculation of the axial ratios the numbers obtained by the use of weights were taken in every case.

Measurements of Di-potassium Chloro-stannite, $K_2SnCl_4.2H_2O$.

Obtuse prism angle, B to B over C.

Crystal measured.	Weight of observation.	Observed angle.	Calculated angle and differences.
			111° 9′ 35″
No. 2, 2 f.	5	111° 13′ 30″	+ 3 55
No. 3, 2 v. g.	10	111 10 30	+ 0 55
No. 4, 2 f.	5	111 11 00	+ 1 25
No. 8, 2 f.	5	111 6 30	— 3 05
No. 11, 1 v. g. and 1 g.	9	111 7 30	— 2 05
Mean,		111 9 48	+ 0 13
Mean with weights,		111 9 36	+ 0 01

Acute prism angle, B to B over D.

			68° 50′ 25″
No. 3, 1 v. g. and 1 g.	9	68° 49′ 00″	— 1 25
No. 5, 1 g. and 1 f.	6	68 51 00	+ 0 35
No. 6, 2 g.	8	68 49 30	— 0 55
No. 8, 2 f.	5	68 51 30	+ 1 05
No. 9, 2 g.	8	68 51 00	+ 0 35
No. 11, 2 v. g.	10	68 51 00	+ 0 35
Mean,		68 50 30	+ 0 05
Mean with weights,		68 50 25	0 00

Angle of macrodome, A to A over top.

			84° 10′ 46″
No. 6, 1 v. g. and 1 f.	7	84° 12′ 00″	+ 1 14
No. 7, 1 g. and 1 p.	3	84 6 00	— 4 46
No. 8, 1 v. g. and 1 f.	7	84 11 00	+ 0 14
No. 9, 1 v. g. and 1 g.	9	84 10 30	— 0 16
No. 11, 2 g.	8	84 11 30	+ 0 44
Mean,		84 10 12	— 0 34
Mean with weights,		84 10 46	0 00

Angle from prism to macropinacoid, B to C.

			145° 34′ 48″
No. 2, 2 g.	8	145° 37′ 30″	+ 2 42
No. 3, 1 v. g. and 1 g.	9	145 35 30	+ 0 42
No. 5, 2 p.	1	145 29 00	— 5 48
No. 9, 1 f. and 1 p.	2	145 37 00	+ 2 12
No. 11, 1 v. g. and 1 p.	4	145 36 00	+ 1 12
Mean,		145 35 00	+ 0 12
Mean with weights,		145 36 06	+ 1 18

Angle from prism to brachypinacoid, B to D.

				124° 25′ 12″
No. 3, 1 v. g. and 1 g.	9	124°	24′ 30″	— 0 42
No. 4, 1 f. and 1 p.	2	124	28 00	+ 2 48
No. 6, 1 v. g. and 1 g.	9	124	23 30	— 1 42
No. 8, 2 f.	5	124	25 00	— 0 12
No. 9, 2 g.	8	124	24 00	— 1 12
No. 11, 1 v. g. and 1 g.	9	124	25 30	+ 0 18
Mean,		124	25 05	— 0 07
Mean with weights,		124	24 38	— 0 34

Angle from prism to macrodome, B to A.

				127° 44′ 47″
No. 3, 2 v. g.	10	127°	46′ 00″	+ 1 13
No. 4, 1 f. and 1 p.	2	127	43 30	— 1 17
No. 6, 1 g. and 1 f.	6	127	43 30	— 1 17
No. 8, 2 v. g.	10	127	43 00	— 1 47
No. 9, 2 f.	5	127	43 00	— 1 47
No. 11, 2 v. g.	10	127	44 30	— 0 17
Mean,		127	43 55	— 0 52
Mean with weights,		127	44 08	— 0 39

From the angles 68° 50′ 25″ and 84° 10′ 46″ the value of the axes may be calculated, and the axial ratio is found to be

a : b : c as 0.685231 : 1 : 0.758634.

Measurements of Di-ammonium Chloro-stannite,
$(NH_4)_2SnCl_4.2H_2O$.

Obtuse prism angle, B to B over C.

				111° 39′ 30″
No. 15, 2 p.	1	111°	37′ 00″	— 2 30
No. 16, 2 p.	1	111	43 00	+ 3 30
No. 19, 2 p.	1	111	39 00	— 0 30
No. 20, 2 f.	5	111	39 00	— 0 30
No. 21, 1 v. g. and 1 f.	7	111	39 00	— 0 30
No. 22, 2 f.	5	111	40 30	+ 1 00
Mean,		111	39 35	+ 0 05
Mean with weights,		111	39 28	— 0 02

Acute prism angle, B to B over D.

				68° 20′ 30″
No. 13, 2 f.	5	68°	21′ 30″	+ 1 00
No. 15, 2 f.	5	68	23 00	+ 2 30
No. 16, 2 p.	1	68	21 00	+ 0 30
No. 17, 2 p.	1	68	22 30	+ 2 00
No. 18, 2 p.	1	68	25 00	+ 4 30
No. 19, 2 f.	5	68	27 00	+ 6 30
No. 20, 2 f.	5	68	20 30	0 00
No. 21, 2 v. g.	10	68	16 00	— 4 30
Mean,		68	22 04	+ 1 34
Mean with weights,		68	20 27	— 0 03

Angle of macrodome, A to A over top.

			84° 7′ 43″
No. 13, 1 g. and 1 p.	3	84° 11′ 00″	+ 3 17
No. 15, 2 f.	5	84 11 00	+ 3 17
No. 16, 1 f. and 1 p.	2	84 05 00	— 2 43
No. 17, 1 g. and 1 p.	3	84 09 00	+ 1 17
No. 19, 2 f.	5	84 07 00	— 0 43
No. 20, 1 v. g. and 1 f.	7	84 07 00	— 0 43
No. 21, 2 f.	5	84 04 30	— 3 13
Mean,		84 07 47	+ 0 04
Mean with weights,		84 07 43	0 00

Angle from prism to brachypinacoid, B to D.

			124° 10′ 15″
No. 13, 2 f.	5	124° 13′ 30″	+ 3 15
No. 15, 2 f.	5	124 13 00	+ 2 45
No. 16, 2 p.	1	124 12 30	+ 2 15
No. 17, 2 p.	1	124 13 00	+ 2 45
No. 18, 1 g. and 1 p.	3	124 12 30	+ 2 15
No. 19, 1 v. g. and 1 f.	7	124 05 00	— 5 15
No. 20, 1 v. g. and 1 f.	7	124 09 00	— 1 15
Mean,		124 11 13	+ 0 58
Mean with weights,		124 10 07	— 0 08

Angle from prism to macrodome, B to A.

			127° 53′ 46″
No. 15, 1 g. and 1 f.	6	127° 55′ 30″	+ 1 44
No. 16, 2 f.	5	127 55 30	+ 1 44
No. 17, 1 f. and 1 p.	2	127 55 00	+ 1 14
No. 19, 1 f. and 1 p.	2	127 57 00	+ 3 14
No. 20, 2 v. g.	10	127 52 00	— 1 46
Mean,		127 55 00	+ 1 14
Mean with weights,		127 54 11	+ 0 25

The axes may be calculated from the angles 68° 20′ 30″ and 84° 07′ 43″.

The axial ratio is : a : b : c as 0.678855 : 1 : 0.752244.

Measurements of Di-ammonium Bromo-stannite, $(NH_4)_2SnBr_4.2H_2O$.

Obtuse prism angle, B to B over C.

			111° 43′ 14″
No. 23, 2 f.	5	111° 43′ 00″	— 0 14
No. 24, 2 f.	5	111 41 00	— 2 14
No. 25, 2 f.	5	111 46 00	+ 2 46
No. 26, 2 f.	5	111 41 00	— 2 14
No. 27, 2 f.	5	111 40 00	— 3 14
No. 28, 1 g. and 1 f.	6	111 45 00	+ 1 46
Mean,		111 42 40	— 0 34
Mean with weights,		111 42 44	— 0 30

Acute prism angle, B to B over D.

				68° 16′ 46″
No. 23, 2 f.	5	68°	15′ 00″	— 1 46
No. 24, 2 p.	1	68	18 00	+ 1 14
No. 25, 2 f.	5	68	17 30	+ 0 44
No. 26, 1 f. and 1 p.	2	68	13 30	— 3 16
No. 27, 2 f.	5	68	19 30	+ 2 44
No. 28, 2 f.	5	68	15 00	— 1 46
Mean,		68	16 00	— 0 36
Mean with weights,		68	16 16	— 0 30

Angle of macrodome, A to A over top.

				84° 17′ 42″
No. 23, 1 v. g. and 1 p.	4	84°	20′ 30″	+ 2 48
No. 25, 2 g.	8	84	21 00	+ 3 18
No. 26, 2 g.	8	84	20 00	+ 2 18
No. 28, 2 f.	5	84	18 00	+ 0 18
No. 29, 2 v. g.	10	84	21 00	+ 3 18
No. 30, 2 g.	8	84	15 30	— 2 12
No. 31, 1 v. g. and 1 g.	9	84	14 00	— 3 42
No. 32, 2 g.	8	84	16 30	— 1 12
No. 33, 2 g.	8	84	14 00	— 3 42
Mean,		84	17 50	+ 0 08
Mean with weights,		84	17 42	0 00

Angle from the prism to the macrodome, B to A.

				127° 51′ 15″
No. 23, 1 v. g. and 1 p.	4	127°	54′ 00″	+ 2 45
No. 26, 1 g. and 1 p.	3	127	51 30	+ 0 15
No. 27, 2 f.	5	127	53 00	+ 1 45
No. 28, 2 f.	5	127	51 00	— 0 15
No. 29, 1 v. g. and 1 f.	7	127	51 00	— 0 15
No. 30, 2 g.	8	127	51 00	— 0 15
Mean,		127	51 55	+ 0 40
Mean with weights,		127	51 47	+ 0 32

Calculating the axial ratios from the angles 68° 16′ 46″ and 84° 17′ 42″, we have a : b : c as 0.678063 : 1 : 0.749178.

Measurements of Di-potassium Bromo-stannite, $K_2SnBr_4.2H_2O$.

Obtuse prism angle, B to B over C.

				111° 20′ 52″
No. 34, 2 f.	5	111°	21′ 00″	+ 0 08
No. 35, 2 p.	1	111	20 00	— 0 52
No. 36, 1 f. and 1 p.	2	111	16 00	— 4 52
No. 37, 1 f. and 1 g.	6	111	18 30	— 2 22
No. 38, 2 f.	5	111	24 00	+ 3 08
No. 39, 2 f.	5	111	20 00	— 0 52
No. 40, 1 f. and 1 p.	2	111	20 00	— 0 52
Mean,		111	19 59	— 0 53
Mean with weights,		111	20 12	— 0 40

Acute prism angle, B to B over D.

			68° 39′ 08″
No. 34, 1 f. and 1 p.	2	68° 35′ 00″	— 4 08
No. 36, 1 f. and 1 g.	6	68 45 30	+ 6 22
No. 37, 1 f. and 1 p.	2	68 40 30	+ 1 22
No. 38, 2 f.	5	68 36 00	— 3 08
No. 39, 1 v. g. and 1 g.	9	68 36 00	— 3 08
No. 41, 2 f.	5	68 38 30	— 0 38
No. 42, 2 p.	1	68 40 00	+ 0 52
Mean,		68 38 34	— 0 34
Mean with weights,		68 38 28	— 0 40

Angle of macrodome, A to A over top.

			84° 52′ 46″
No. 37, 2 p.	1	84° 48′ 00″	— 4 46
No. 39, 1 f. and 1 g.	6	84 54 00	+ 1 14
No. 42, 2 f.	5	84 53 00	+ 0 14
Mean,		84 51 40	— 1 06
Mean with weights,		84 53 05	+ 0 19

Angle from prism to pyramid, B to E.

			142° 56′ 48″
No. 37, 2 p.	1	142° 55′ 30″	— 1 18
No. 38, 2 p.	1	143 01 00	+ 4 12
No. 39, 1 f. and 1 g.	6	142 52 30	— 3 18
No. 40, 2 f.	5	143 01 00	+ 4 12
No. 42, 2 p.	1	142 54 00	— 2 18
No. 43, 2 p.	1	142 55 00	— 1 18
Mean,		142 56 45	— 0 03
Mean with weights,		142 56 48	0 00

Calculating the value of the axes from the angles 68° 39′ 08″ and 142° 56′ 48″ we get:

a : b : c as 0.682822 : 1 : 0.746746.

Collecting these results we have the following tabular statement:

	A.	C.	$\infty P \wedge \infty P$.	$P\bar{\infty} \wedge P\bar{\infty}$.
$K_2SnCl_4.2H_2O$	0.685231	0.758634	68° 50′ 25″	84° 10′ 46″
$(NH_4)_2SnCl_4.2H_2O$	0.678855	0.752244	68 20 30	84 07 43
$(NH_4)_2SnBr_4.2H_2O$	0.678063	0.749178	68 16 46	84 17 42
$K_2SnBr_4.2H_2O$	0.682822	0.746746	68 39 08	84 52 46

The changes in the value of the axes may be farther tabulated as follows:

In passing	The change in A is	The change in C is
From $K_2SnCl_4.2H_2O$ to $K_2SnBr_4.2H_2O$	— 0.002409	— 0.011888
From $(NH_4)_2SnCl_4.2H_2O$ to $(NH_4)_2SnBr_4.2H_2O$	— 0.000792	— 0.003066
From $K_2SnCl_4.2H_2O$ to $(NH_4)_2SnCl_4.2H_2O$	— 0.006376	— 0.006390
From $K_2SnBr_4.2H_2O$ to $(NH_4)_2SnBr_4.2H_2O$	— 0.004759	+ 0.002432

From this table we see that the change in the halogen or acid element appears to affect the vertical axis much more than it does the lateral axis, and that the change is much less marked with the ammonium salt than with the potassium salt.

While the change in the alkali or basic element affects both axes nearly the same amount in the case of the chlorides, and the lateral axis more in the case of the bromides, we find that the vertical axis is *increased* instead of diminished in passing from $K_2SnBr_4.2H_2O$ to $(NH_4)_2SnBr_4.2H_2O$. The A and C axes are both nearer unity in the chlorides than in the bromides, and in general the potassium salts approach the regular form more closely than the ammonium salts.

It is hoped to increase the number of salts in this series by preparing the rubidium and caesium salts if possible; with the additional data thus obtained, perhaps the law governing the change in the axes will be more apparent.

Notes upon Cuprous Double Halide Salts.

Mitscherlich[1] has prepared and described the salt $Cu_2Cl_2.4KCl$ or $CuCl.2KCl$.

This salt is of interest on account of the unusually large proportion of potassium chloride present, causing it to be an exception to the rule governing the composition of the other double chlorides.

This salt may be prepared by dissolving freshly made cuprous chloride in a hot potassium chloride solution, filtering the solution while hot into a flask or some vessel from which the air can be excluded, until the vessel is completely full, and allowed to cool tightly closed. If the solution contains an excess of cuprous chloride it will crystallise out alone when the solution cools.

[1] Ann. chim. phys. **73** (1840), 384.

Otherwise, after standing a few days, better in the dark, clear, colorless, apparently monoclinic crystals are formed. These crystals may grow to a considerable size, being transparent, with opaque white streaks in them. When exposed to the air they are rapidly decomposed, forming a green powder.

Several specimens of these crystals were prepared and analysed, care being taken to dry and weigh them rapidly before material change in their composition could take place. The results confirm the correctness of the formula assigned by Mitscherlich.

	Found.				
	A.	B.	C.	D.	Calculated.
Cu	25.34 p. ct.	25.28 p. ct.	25.24 p. ct.	25.37 p. ct.	25.56 p. ct.
K	30.85	31.29	...	...	31.50
Cl	42.05	42.75	42.66	...	42.94

Considering the difficulties of starting with pure samples of the salt, a closer approach to the theoretical percentage could not be expected.

All descriptions of this salt heretofore given have described it as being isometric in its crystallisation. The crystals obtained in the above described manner are evidently not isometric, they are perhaps orthorhombic, but probably monoclinic.

The corresponding double bromide CuBr.2KBr was made by using cuprous bromide and potassium bromide in exactly the same way that the double chloride was prepared.

Crystals evidently isomorphous with the crystals of the double chloride were obtained.

These gave upon analysis:

	Found.	Calculated.
Cu	16.20 per cent.	16.62 per cent.
Br	62.41	62.92

Here then appears to be a well marked exception to the rule already given.

A careful study of the cuprous salts will soon be undertaken.

Conclusion.

Concerning the other exceptions to the rule mentioned on page 9, I may add that the salt $MnF_2.4KF$ cannot be prepared according to the directions given by Nickles. Mr. C. H. Herty, working in this laboratory, has shown that the salt $PbI_2.4KI$, described by

Boulay, does not exist. And Mr. C. E. Saunders, also working in this laboratory, has been unable to obtain the salt $SbCl_3.6CsCl$, described by Godefroy. The work given in this paper disproves the existence of the salt $SnCl_4.4KCl.3H_2O$, described by Poggiale. This leaves the salt $CuCl_2.2KCl$ as the only known exception to the rule. Until this salt has been the subject of further study, little can be said concerning it.

Biographical Sketch.

George M. Richardson was born at Springfield, Ohio, October 3, 1863. He attended the public schools for a short time, and then went to Cook Academy in Havana, N. Y., where he remained from 1876–78. He was in the preparatory department of Antioch College, Yellow Springs, Greene Co., Ohio, from 1879–81, and at Ulrich's Preparatory School in Bethlehem, Pa., from 1881 to 1882.

In the fall of 1882 he entered the Lehigh University, and there pursued the course in chemistry, graduating in June, 1886.

In October, 1886, he entered the Johns Hopkins University, studying chemistry, with mineralogy and geology as subsidiary subjects.

After remaining here two years he returned to the Lehigh University as Instructor in Chemistry, and after a year of teaching, obtained leave of absence in order to return to the Johns Hopkins University, and there he continued the courses which he had previously taken up, during the year 1889–90.